

Effect of elemental sulfur application on ammonia volatilization from surface applied urea fertilizer to calcareous sandy soils

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Abstract

Widespread acceptance of urea was delayed in part due to its greater potential for nitrogen (N) loss via ammonia volatilization. Elemental sulfur (S⁰) at rates of 0, 1, 5 and 10 t ha⁻¹ combined with or without urea and inoculation of *Paracoccus versutus* (Pv) were tested to determine NH₃-N volatilization from urea in sandy calcareous soils of Masafi-1 and Masafi-2. Daily NH₃-N loss was measured up to 29 days after surface urea application in both soils using the closed dynamic airflow system. Total NH₃-N volatilizations from urea-treated soils were 22.15 to 29.74 % of applied N in Masafi -1 and Masafi -2 soils, respectively. Application of S⁰ had a positive influence on reducing NH₃-N volatilization from surface applied urea. In both soils significant reductions in NH₃-N volatilization were observed in amended soil by S⁰. The result reveals that S⁰ at rates of 1 or 5 t ha⁻¹ and 5 or 10 t ha⁻¹ is required to minimize volatile loss of NH₃-N from surface applied urea in Masafi-1 and Masafi-2 soils, respectively. Application of Pv with or without S⁰ and urea had no positive influence on reduction of NH₃-N volatilization.

Keywords: Ammonia volatilization, elemental sulfur, sandy calcareous soils, urea

Abbreviations: DAI-days after incubation, N-nitrogen, Pv- *Paracoccus versutus*, S-sulfur, S⁰-elemental sulfur, U-urea, UAE-United Arab Emirates

Introduction

Urea is the cheapest form of granular nitrogen, widely used for crop plants (Dong et al., 2009) and accounts for more than 50% of the world's nitrogenous fertilizers (Schwab and Murdock, 2005). However, one of the great disadvantages of urea among nitrogenous fertilizers is its volatile property which causes large losses of urea to the environment. The loss of urea is highly dependent on the rate of hydrolysis which in turn is influenced by soil temperature, soil moisture, relative humidity, wind speed, rainfall pattern, cation exchange capacity, H⁺ ion buffering capacity, CaCO₃ content, organic matter content and N source (Jones et al., 2007) and urease activity as well (Watson et al., 2008). Ammonia volatilization is directly related to soil pH near the fertilizer droplet or granule, which largely determines the ratio of NH₃ to NH₄⁺ in the soil solution (Jones et al., 2007). Alkaline soils (pH>8.2 or higher) have proven to increase urea hydrolysis (Christopher et al., 2010) and this condition occurs in calcareous soils, or where the breakdown of the N fertilizer produces alkaline conditions. In addition, the formation of the hydroxide ions can cause soils around the applied urea particle to have a pH around 9.0 which increases ammonia volatilization (McInnes et al., 1986). When surface soil pH value is greater than 7.0, volatilization of NH₃-N fertilizer is significantly increased. The urease-mediated reaction of soil-applied urea with H₂O results in rapid conversion to NH₄⁺. In this reaction, H⁺ ions are consumed and NH₄⁺ and HCO₃⁻ are produced, causing the soil pH, at the

reaction site to increase. Soil pH change depends on initial pH, net inputs of acid or alkali, and the soil's pH buffering capacity (Bloom, 2000) and soils with a larger H⁺ ion buffering capacity have been shown to also retain more NH₃ (Izaurrealde et al., 1987). The NH₃ losses due to urea hydrolysis may reach as much as 80% of the total N applied under field conditions (Gould et al., 1986). Ammonia volatilization is the loss of N to the atmosphere through conversion of the ammonium ion to ammonia gas (NH₃). Ammonium is an available source of N for plant while ammonia is not (Bardy and Weil, 2002). Ammonia loss from unamended urea varies with soil type and temperature, ranging from 8.2 to 31.9% of the applied N (Watson et al., 2008). Nitrogen loss through ammonia volatilization on calcareous soils is a common concern when NH₃-N is applied to the soil surface and remains there without incorporation into the soil. Therefore, in an application of dry fertilizer containing NH₃-N, the fertilizer should be moved into the root zone through irrigation or mechanical incorporation (Jones et al., 2007). This means, timing and method of urea application is a crucial factor to minimize volatilization loss. A substantial amount of N losses can occur if urea is not incorporated into the soil soon after application. The amount of surface residue and time between urea application and precipitation are also critical. Although the influence of the individual factors on NH₃ volatilization has been established,

Table 1. Physicochemical properties of Masafi-1 and Masafi-2 soils

Soil properties	Masafi soils-1	Masafi soils-2
Texture		
Sand (%)	87.50	87.50
Silt (%)	5.00	5.00
Clay (%)	7.50	7.50
Total carbonate (%)	24.53	26.07
EC (dSm ⁻¹)	9.49	12.68
pH	7.58	7.70
Cations (mq L⁻¹)		
Ca	25.00	38.20
Mg	34.20	39.20
Na	53.80	56.20
K	7.520	11.94
Anions (mq L⁻¹)		
Cl	46.80	52.00
HCO ₃	20.40	8.40
SO ₄	0.64	6.20
Mg:Ca Ratio	1.37	1.03

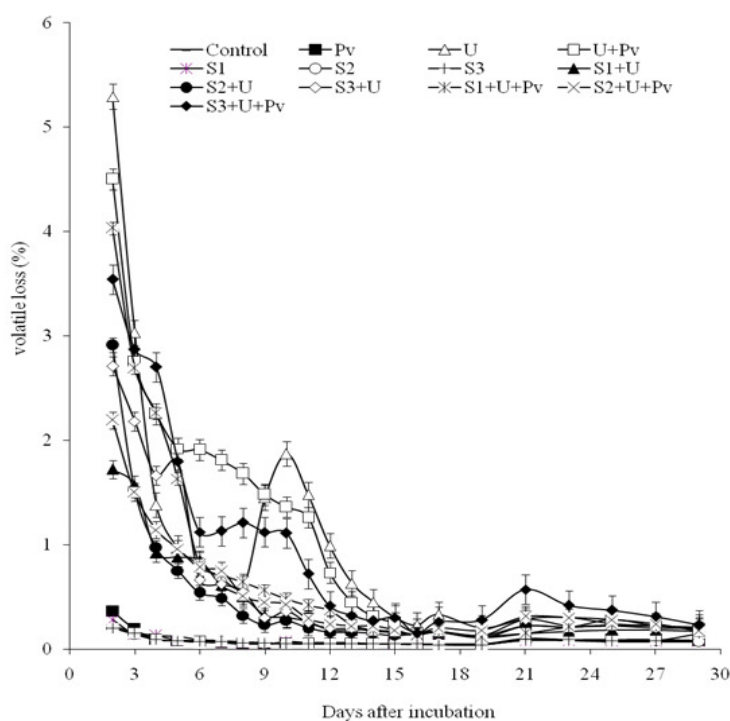


Fig. 1. Ammonia volatilization from surface applied urea as affected by elemental S and *Pv* in Masafi-1 soils
 S1-elemental sulfur 1 t/ha, S2-elemental sulfur 5 t/ha, S3-elemental sulfur 10 t/ha, U- urea, *Pv*-*Paracoccus versutus*; Error bars denotes LSD value

the prediction of actual N volatilization losses under a given set of soil and environmental factors can seldom be achieved, due to the complex interactions (Ping et al., 2000). Fertilizer is often applied when field conditions are not optimal, particularly in large scale operations. Thus, crop yield is reduced and extra costs are incurred from additional N fertilizer due to rapid volatile loss of ammonia. Therefore, economic efficiency of cropping systems is reduced due to volatile loss of ammonia. The use of inhibitors can decrease the localized zones of high pH common with untreated urea

(Schwab and Murdock, 2005; McCarty et al., 1989), for example N losses can be reduced by the use of a urease inhibitor added to the fertilizer. The use of NPBT allows urea to be used more efficiently and the cost effective delivery vehicle for nitrogen soil amendment, per unit of nitrogen, occurs at a lower cost (Watson et al., 2008). Approaches have been taken to decrease the NH₃ loss by using S⁰ that retard hydrolysis of urea by reducing the activities of urease (Abdou, 2001; Al-Kanani et al., 1994; McCarty et al., 1989; Broadbent et al., 1985). Elemental S has been used for many

Table 2. Total ammonia volatilization and reduction of ammonia volatilization from surface applied urea as affected by elemental sulfur and *Paracoccus versutus*

Treatment	Masafi Soil-1		Masafi Soil-2	
	NH ₃ -N loss (%)	Reduction in NH ₃ -N loss** (%)	NH ₃ -N loss (%)	Reduction in NH ₃ -N loss (%)
Control (*S ⁰ 0+U0+Pv0)	1.92	-	2.08	-
U	22.15	-	29.74	-
Pv	2.04	-	2.36	-
U+Pv	24.47	- 10.47	39.04	-31.27
S ⁰ 1 t ha ⁻¹	1.86	8.82	2.20	6.78
S ⁰ 5 t ha ⁻¹	1.80	11.76	2.41	-2.12
S ⁰ 10 t ha ⁻¹	1.83	10.29	2.28	3.39
S ⁰ 1 t ha ⁻¹ +U	10.02	54.76	20.31	31.71
S ⁰ 5 t ha ⁻¹ +U	10.45	52.82	17.95	39.64
S ⁰ 10 t ha ⁻¹ +U	13.50	39.05	15.49	47.92
S ⁰ 1 t ha ⁻¹ +U+Pv	16.03	27.63	19.40	34.77
S ⁰ 5 t ha ⁻¹ +U+Pv	11.88	46.37	21.17	28.82
S ⁰ 10 t ha ⁻¹ +U+Pv	21.32	03.75	21.33	28.29
LSD 0.05	0.88	-	1.25	-

*S⁰= elemental sulfur, U-urea, Pv-*Paracoccus versutus*, ** % Reduction in NH₃-N loss = (A-B/A) x 100, where A = % NH₃-N loss in U treatment, B = % NH₃-N loss in S⁰, S⁰+U, S⁰+U+Pv treatments.

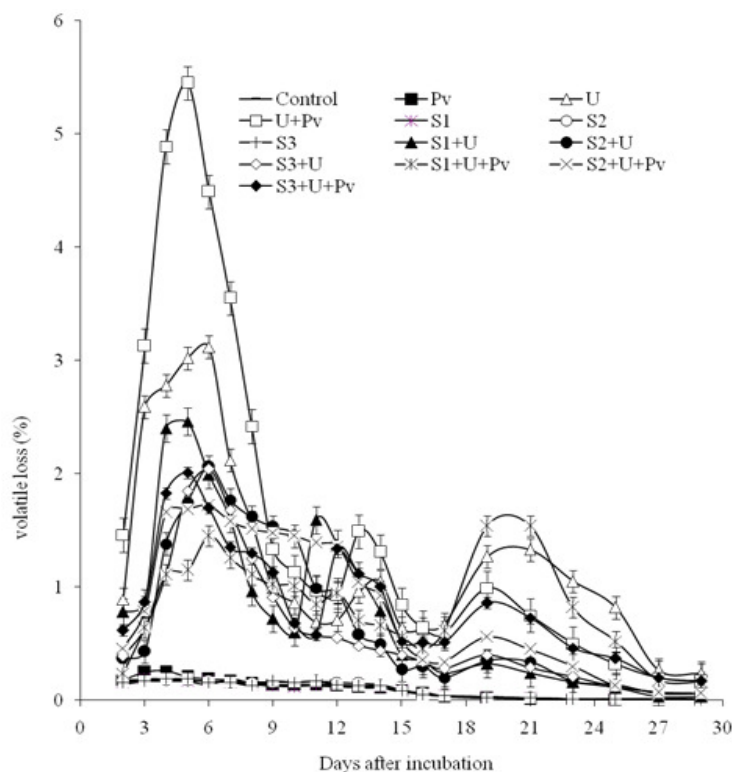


Fig. 2. Ammonia volatilization from surface applied urea as affected by elemental S and Pv in Masafi-2 soils
 S1-elemental sulfur 1 t/ha, S2-elemental sulfur 5 t/ha, S3-elemental sulfur 10 t/ha, U- urea, Pv-*Paracoccus versutus*; Error bars denotes LSD value

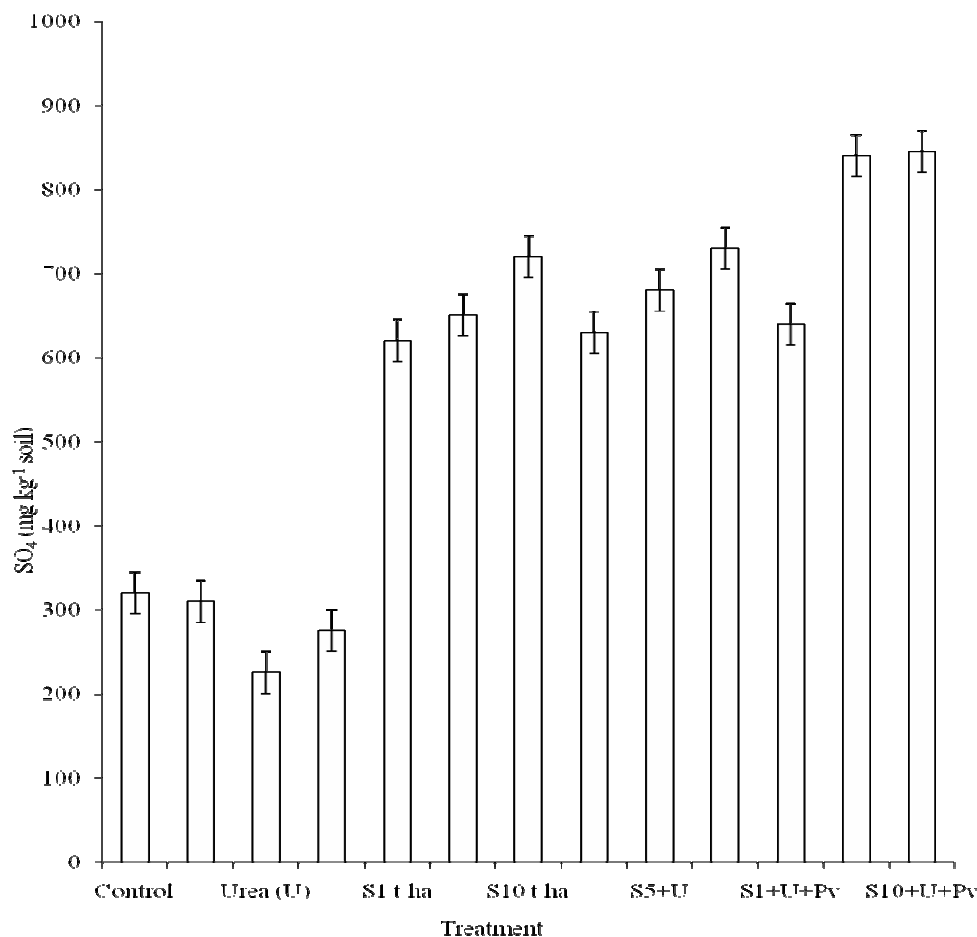


Fig. 3. Sulfate concentration as affected by elemental S, urea and Pv inoculation in Masafi-1 soils
 S=elemental sulfur, U= urea, Pv=*Paracoccus versutus*
 Error bar denotes LSD value at 0.05 of probability

years in the reclamation and improvement of sodic and calcareous soils (Abdel Fattah et al., 1990; Wassif et al., 1993). Recently, more attention has been given to S application to soils due to its favorable effects in promoting nutrient availability in soils (Saleh, 2001; El-Fakharani, 1995). Application of S⁰ for the amendment of alkaline and/or calcareous soils has received little attention, as an inhibitor for ammonia volatilization. Therefore, this study was undertaken to determine the rate of NH₃-N volatilization from surface applied area as affected by varying rates of S⁰ application combined with or without urea and Pv inoculation in sandy calcareous soils in United Arab Emirates (UAE).

Materials and methods

Experimental design

The study was carried out at laboratory of Aridland Agriculture, College of Food Systems, UAE University. Sandy calcareous soil was collected from two locations of Masafi region, Al Fujairah, UAE (25°18'48"N 56°9'46"E) which was designated by Masafi-1 and Masafi-2. Elemental S at rates of 0, 1, 5 and 10 t ha⁻¹ was tested combined with or without urea and *Paracoccus versutus*. Urea was used at rates

of 0 and 200 kg ha⁻¹. The treatment arrangements are as follows: Control (S⁰0+U0+Pv0), urea (U), *Paracoccus versutus* (Pv), U+Pv, S⁰ 1 t ha⁻¹, S⁰ 5 t ha⁻¹, S⁰ 10 t ha⁻¹, S⁰ 1 t ha⁻¹+U, S⁰ 5 t ha⁻¹+U, S⁰ 10 t ha⁻¹+U, S⁰ 1 t ha⁻¹+U+Pv, S⁰ 5 t ha⁻¹+U+Pv and S⁰ 10 t ha⁻¹+U+Pv. The experiment was conducted under completely randomized design with three replications.

Management practices

A proportion of soil was separated and sieved through 1-mm stainless steel sieve and stored in plastic bags for physicochemical analysis. Soil pH was determined from the prepared soil suspension (1:2.5 soil water ratios) by using combined pH meter model 900A (Thermo Orion, Ontario, Canada) (Thomas, 1996). Electrical conductivity (EC) was measured by the saturation extracts of soil samples using Orion model 120 microprocessor conductivity meters (Thermo Scientific, USA). Water soluble cations (Ca, Mg, Na, and K) and anions (Cl, HCO₃, CO₃ and SO₄) were determined as per the methods recommended in Page et al., (1982). Physicochemical properties of the soil are presented in Table 1. Elemental S powder (particle size <150 μm) was collected from TAKREER Company, Ruwais, Abu Dhabi,

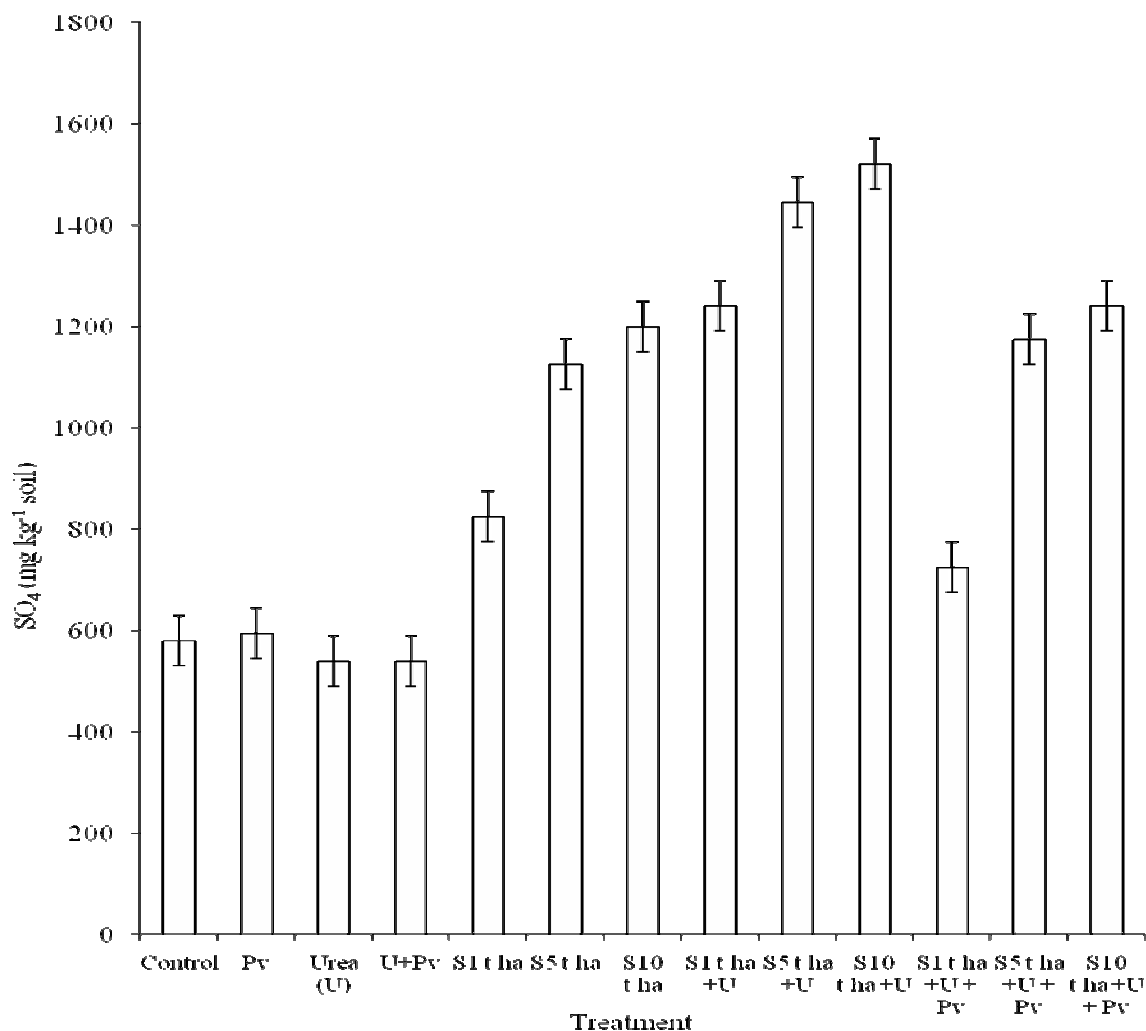


Fig 4. Sulfate concentration as affected by elemental S, urea and *Pv* inoculation in Masafi-2 soils
 S- elemental sulfur, U-urea, *Pv*-*paracoccus versutus*
 Error bar denotes LSD value at 0.05 of probability

UAE and added as per treatment schedule. Commercial grade of granular urea fertilizer was used as a source of N. Local sulfur-oxidizing bacteria *Paracoccus versutus* (CBS 114155) was used which was previously isolated from the western regions of the UAE (El-Tarabily et al., 2006). Soils were air-dried before being used in the experimental glass bottles. Under ambient laboratory conditions (23-25°C), a triplicate of 150 g soil were mixed thoroughly with 0.0, 0.502, 2.510 and 5.020 g of S⁰ powder corresponding to 0, 1, 5 and 10 t ha⁻¹ and the mixtures were transferred into 1000-mL glass bottles (surface area 50.26 m²) then urea fertilizer (0.258 g) was added on the soil surface at the rate of 200 kg ha⁻¹. After addition of urea fertilizer and *Pv*, the soil samples were wetted with distilled water using automatic burette and maintained to field capacity (12.0%).

Measurement of volatilization

A closed dynamic airflow system (Purakayastha and Katyal, 1998) was used to measure the NH₃-N volatilization. All

bottles were connected to the air flow system immediately after soil wetting and the outlets from each bottle was immersed in a boric acid (2%) mixed indicator solution to capture the NH₃-N volatilized from soil surfaces (Al-Kanani et al., 1994). The inlet compressed air flow was first passed to bubble through distilled water to produce humidified air, which then passed to the bottles with fixed rate. Boric acid-mixed indicator traps were replaced every 24 hrs for a period of 29 days after incubation (DAI) for both soils and the ammonia was determined by titrating with 0.01M H₂SO₄ solution (Bundy and Meisnger, 1994). The amounts of volatilized NH₃-N were calculated as percent of the applied urea-N.

Statistical analysis

Statistical analysis was carried out by one-way ANOVA using general linear model to evaluate significant differences between means at 95% level of confidence (SAS, 2003). Further statistical validity of the differences among treatment

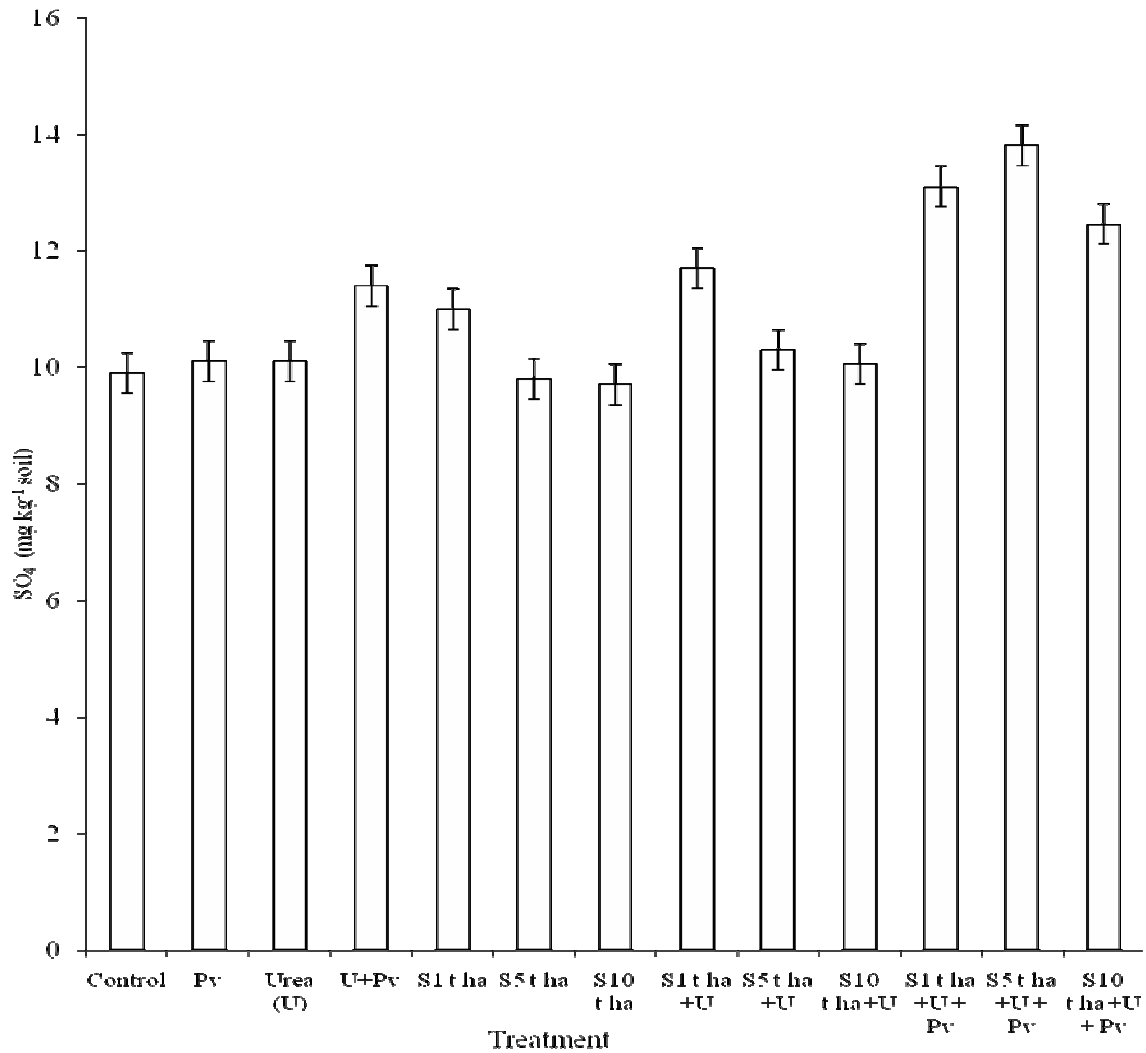


Fig 5. Electrical conductivity as affected by elemental S, urea and Pv inoculation in Masafi-1 soils
 S-elemental sulfur, U-urea, Pv-*Paracoccus versutus*
 Error bar denotes LSD at 0.05 of probability

means was determined using the least significant differences (LSD) comparison method.

Results and discussion

Soil properties had significant influence on NH₃-N volatilization. Masafi-1 soils have higher concentration of Ca/Mg ratio and HCO₃ and lower concentration of EC, SO₄, Ca and Mg. On the contrary Masafi-2 soils have lower concentration of Ca/Mg ratio and HCO₃ and higher concentration EC, SO₄, Ca and Mg that enhanced the rate of NH₃-N volatilization (Table 1). The NH₃-N volatilization was reduced from surface applied urea by amendment of S⁰ in both soils. The results clearly indicates that the rate of NH₃-N volatilization is directly associated with physiochemical properties of soil such as Ca/Mg ratio, EC, HCO₃, SO₄, Ca and Mg concentration in soil (Table 1). The pattern of NH₃-N

volatilization differed among the treatment variables. The daily highest rate of NH₃-N volatilization (5.29%) was observed in urea treated soil followed by urea with Pv (4.50%) and S⁰ at the rate of 1 t ha⁻¹ with urea and Pv. The peak NH₃-N% volatilization was observed at 2 DAI and thereafter reduced slowly in most of the treatments in Masafi-1 soils (Fig. 1). The NH₃-N volatilization significantly reduced by addition of S⁰ at rates of 1, 5 and 10 t ha⁻¹ followed by control treatment and slowly declined up to 19 DAI and thereafter rose slightly but significantly lower than other treatments in Masafi-1 soils (Fig. 1). Minimum NH₃-N volatilization was observed in S⁰ amended soil regardless of levels of S⁰ and control treatment. In Masafi-1 soils, NH₃-N volatilization of control treatment decreased gradually up to 19 DAI then rose again and continued at same trend up to the end of incubation period (Fig. 1). In Masafi-1 soils inoculated by Pv, NH₃-N volatilization decreased from the second day

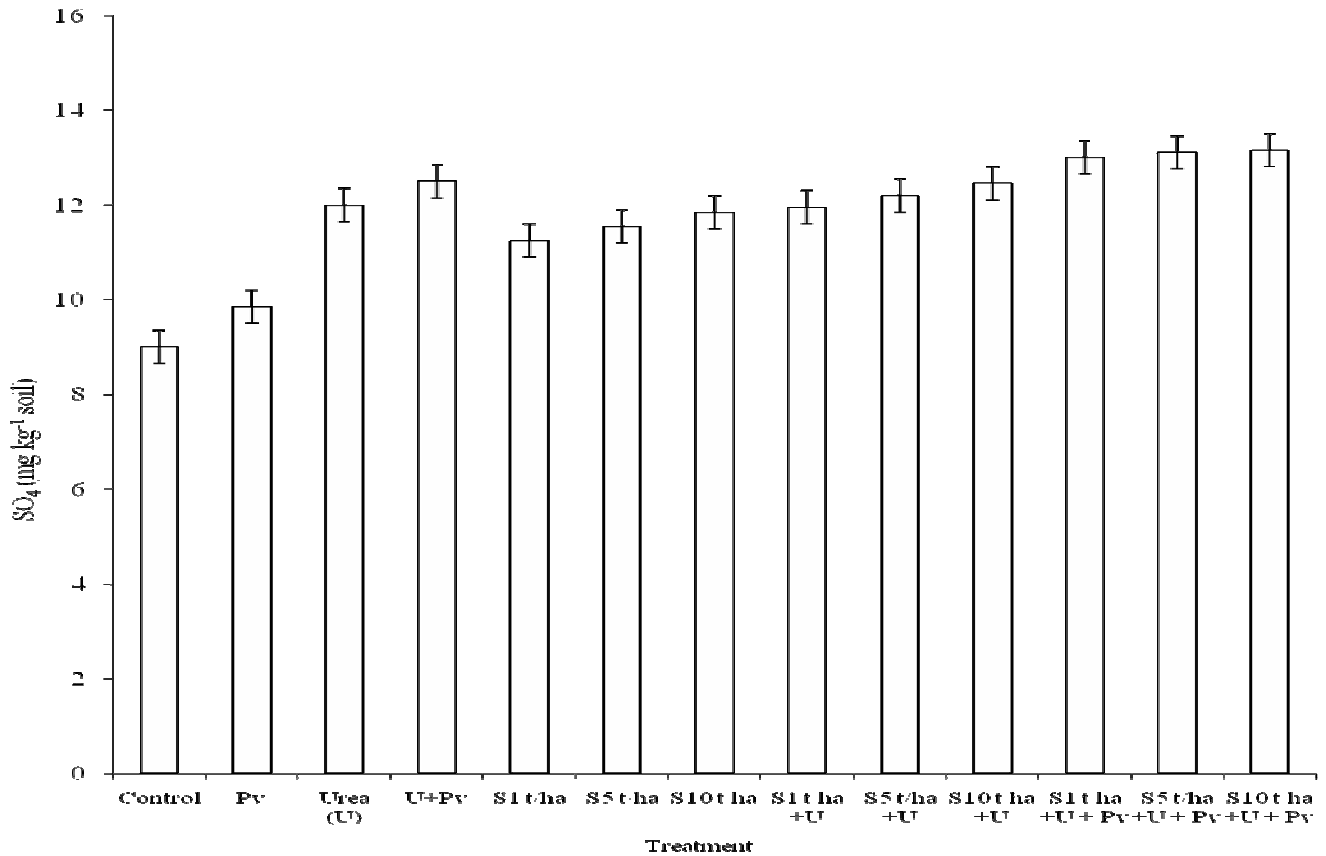


Fig. 6. Electrical conductivity as affected by elemental S, urea and Pv inoculation in Masafi - 2 soils
S-elemental sulfur, **U**- urea, **Pv**-*Paracoccus versutus*
 Error bar denotes L SD at 0.05 of probability

of incubation and then gradually reduced up to 19 days and again slightly rose while in Masafi-2 soils NH₃-N slightly rose up to 3 DAI and thereafter slowly declined up to end of the incubation period. The present findings are in agreement with Dong et al., (2009). They reported that NH₃ losses peaked on day 3 after urea application while soil amended with wheat and corn straw plus urea shifted the peak of NH₃ losses 1 day ahead. In Masafi-2 soils, the highest rate of NH₃-N (5.45%) volatilization was observed at 4 DAI in U+Pv inoculated soil followed by urea treated soil (3.12%). The NH₃-N volatilization rate was significantly reduced by addition of S⁰ regardless of levels with urea and Pv inoculated soil. Ammonia-N loss reached peak at 3 to 4 DAI in most of the treatments and thereafter declined gradually up to end of the incubation period (Fig. 2). In Masafi-2 soils, the declining rate of NH₃-N volatilization was a bit different from Masafi-1 soils. The NH₃-N volatilization reached peak at 4 DAI in Pv inoculated soil regardless of S⁰ levels and S⁰ at the rate of 1 t ha⁻¹+U while all other treatments except control treatment reached peak at 5 DAI and thereafter declined gradually except few variations in some treatments in Masafi-2 soils. Regardless of treatment, NH₃-N volatilization was lower in Masafi-2 than Masafi-1 soils. In urea treated soil, decreasing trend of NH₃-N volatilization was observed up to end of the experiment except few variations was observed at 12, 14 and 19 to 23 DAI for both soils. In Masafi-1 soils, concentrations of volatilized NH₃-N reduced in urea-treated samples at 3 DAI but increased in

Masafi-2 soils until 4 to 5 DAI and thereafter declined. In urea-treated soils, the daily amounts of N losses were higher in Masafi -1 than in Masafi -2 soils during whole incubation period (Figs. 1 and 2). The volatile losses of NH₃-N were 22.15 and 29.74 % of applied N from urea treated soils throughout the incubation period in Masafi-1 and Masafi-2 soils, respectively (Table 2). Application of S⁰ significantly reduced NH₃-N volatilization in both soils. The reductions of NH₃-N volatilization loss were 54.76%, 52.82% and 39.05% in Masafi-1 and 31.71%, 39.64% and 47.92% in Masafi-2 soils by combined application of S⁰ at rates of 1, 5 and 10 t ha⁻¹ with urea, respectively (Table 2). In urea-treated soils, inoculation of Pv significantly increased the daily losses of NH₃-N comparing with the non-inoculated samples during incubation period while inoculation of Pv with S⁰ also reduced the ammonia volatilization from urea applied to tested soils, but the rate of reduction was less compared to soils treated with S⁰ only (Table 2). By application of S⁰ inoculated with Pv, the reduction in NH₃-N losses were 27.63%, 46.37% and 3.75% in Masafi-1 and 34.77%, 28.82% and 28.29% in Masafi-2 soils from S⁰ 1 t ha⁻¹+U+Pv, S⁰ 5 t ha⁻¹+U+Pv and S⁰ 10 t ha⁻¹+U+Pv, respectively (Table 2). The results showed that combined application of S⁰ and Pv had no further positive effect on the reduction of ammonia volatilization in both soils. The results of this study also coincidence with Dong et al., (2009) although their soils amended was done by addition of wheat or corn straw with urea. They reported that addition of wheat and corn straw

significantly reduced maximum NH_3 emissions to about 23 to 58% of those from urea only. At the end of soil incubation, SO_4 concentration and EC were determined from saturated soil extracts. Sulfate concentration was significantly varied by the treatment variables. Regardless of treatments, SO_4 concentration was significantly higher in Masafi-2 than Masafi-1 soils (Figs. 3 and 4). The lowest concentration of SO_4 was obtained from urea treated treatment in both soils which had positive influence on NH_3 -N volatilization. The results of SO_4 concentration indicated that SO_4 in saturation extracts increased as the increased rate of S^0 application resulted reduced ammonia volatilization. Application of S^0 had also effect on soil EC and slight differences were observed with increasing S^0 level in both soils. But S^0 with *Pv* resulted increased EC in both soils (Figs. 5 and 6). The results of ammonia volatilization obtained from the incubated soils revealed that application of S^0 played a significant role in reducing the amounts of N losses from soil surfaces. The average NH_3 -N volatilization loss was 1.83% to 2.30% by the application of S^0 while in urea treated soil and loss of NH_3 -N volatilization was much higher in both soils. When urea treated soil amended by S^0 , the rate of NH_3 -N volatilization reduced about 8.65% to 14.25%. In Masafi soil-1, reduction rate of NH_3 -N volatilization was more (13.88 to 14.84%) when soil was amended by S^0 at rates of 1 and 5 t ha⁻¹. While in Masafi soil-2, reduction rate of NH_3 -N volatilization was more (11.79% to 14.25%) when soil was amended by S^0 at rates of 5 and 10 t ha⁻¹. The lower NH_3 -N loss with urea combined with S^0 might be due to neutralization of the alkaline urea microsites by the H_2SO_4 generated by S^0 upon oxidation (Christianson et al., 1993; Blaise and Prasad, 1995) and an acidic environment in the soil (low pH) favors the conversion of NH_3 to NH_4 and thus suppresses NH_3 volatilization (Fenn and Hossner, 1985). The results of ammonia volatilization from urea-treated soils with *Pv* inoculation showed that the rate of NH_3 -N emission from soil surfaces increased in both soils. It is assumed that inoculation of urea-amended soils with non-urease releasing *Pv* increased the NH_3 -N emission comparing with the non-inoculated urea-amended soils. This might be explained by synergistic effect of applied native bacteria in the tested soils resulted in increase the activity of urease producer bacteria (El-Tarably et al., 2006).

Conclusion

In both soils significant reductions in NH_3 -N volatilization were observed and urea treated soil amended by S^0 had significant influence on reducing NH_3 -N volatilization. In Masafi soil-1, S^0 at rates of 1 or 5 t ha⁻¹ and in Masafi soil-2, S^0 at rates of 5 or 10 t ha⁻¹ are to be applied to minimize NH_3 -N loss from surface applied urea. Application of *Paracoccus versutus* with or without S^0 and urea had no positive influence on reduction of NH_3 -N volatilization. The results suggested that the rate of volatilization was higher in Masafi-2 than Masafi-1 soils.

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